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# Ultra-Stable Sintered Silver Die Attach for Demanding High Power/Temperature Applications

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**Abstract:** A novel and simple processing step has been demonstrated to produce thermally stable sintered silver nanoparticles structures. Sintered silver has been investigated as a die attach to resolve the long-standing demand for a reliable material to enable high power/temperature electronics operating above 300 °C. However, it is now a well-known fact that such materials undergo massive microstructural evolution at 250 °C and above, creating doubts about their long-term reliability. Here an additional processing step utilizing oxidizing treatment is demonstrated to immobilize the silver atoms through formation of Ag<sub>2</sub>O. This technique stabilizes sintered silver up to 400 °C, taking advantage of the open pore network to facilitate treatment deep in the material interior.

**Keywords:** Reliability, Aging, Semiconductor Device Packaging, Silver, Nanotechnology.

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## 1. Introduction

One of the most important reliability concerns for high power/temperature electronics is lack of a thermally stable die attach to withstand the new temperature requirement of 300 °C and above [1]. Many different sectors can benefit from such a die attach material such as power electronics, deep-well oil and gas exploration, and implementation of wide-bandgap semiconductors into industry, where even 400 °C operating temperature is a target for near future applications [2]. Two important categories of die attach materials intended for high power/temperature applications are high temperature solders, mainly high gold content solders [3, 4], and Transient Liquid Phase Diffusion Bonding (TLPDB) materials [5]. However, the impetus for research on developing more reliable die attach materials arises from problems with these current materials, which are residual stresses in case of solders [6], and reduction of mechanical strength at elevated temperature in case of TLPDB materials, even if the temperature is well below the melting point of the system intermetallics [7].

A relatively new technique to overcome the issues related to the current die attach materials is sintering of silver nanoparticles to form a porous silver joint between the die and substrate. While this technique has attracted much attention and many research papers have been dedicated to studying this material [8], it has been recently found that this material is strongly susceptible to microstructural variations above 200 °C. As these microstructural changes are normally linked to reduction in mechanical reliability [10, 11], sintered silver materials remain unsuitable for applications above 200 °C unless the internal microstructure can be stabilised as one of the important concerns for its utilisation [8]. No known technique currently exists to stabilise the porous microstructure of pure pressure-less sintered silver above 200 °C. Allowing a second material to be added to help stabilize the silver gives rise to two techniques found in the literature. In one technique, insertion of a gold mesh into the silver nanoparticle paste has resulted in stability

during thermal aging at 600 °C for a minimum of 100 h [12]. In the other technique, addition of SiC to silver paste has been able to increase the thermal stability of the material to at least 250 °C although processing pressure was required [13]. Both techniques complicate the processing steps, and potentially lengthy optimisation of the materials and processing, will need to be followed by extensive testing that pure sintered silver has already undergone, such as shear strength, aging, thermal cycling and flexibility tests [8]. However, in this paper a novel and simple technique for freezing and stabilizing the microstructure of pure sintered silver after the normal processing steps is presented. This technique has shown an increase in microstructural stability to 400 °C.

## 2. Material and Methods

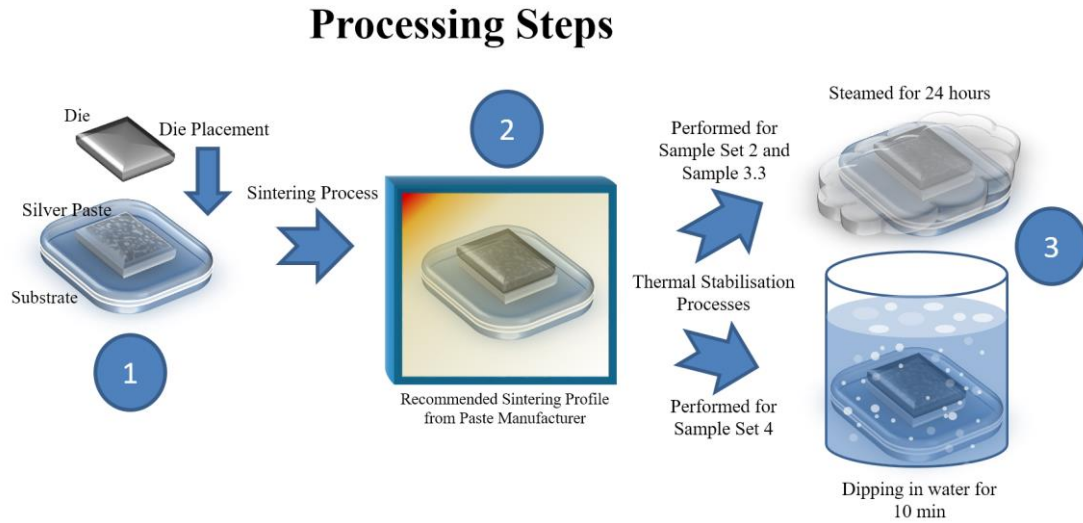
Silver nanoparticle based pastes from NBE Tech, LLC, known as NanoTach® X-Paste and N-Paste, have been utilised in 4 sets of experiments, as shown in Table 1. All the samples were prepared with the pressure-less sintering profile recommended by the paste manufacturer, which involves heating at 7.5 °C/min from room temperature to 260 °C followed by about 30 – 60 minutes at this temperature for X-Paste (for Sample sets 1, 2, 4 and Sample 3.3), and involves a slightly different temperature profile for Samples 3.1 and 3.2 requiring 10 min storage at 275 °C for the final sintering stage. The first two sample sets were sintered on a glass slide and under a cover-slip in order to allow continuous optical observations of microstructure evolution without exposure to air during high temperature ageing. It has been shown previously that the cover-slip does not affect the microstructural evolution of sintered silver [9], making this technique ideal for exploring continuous evolution inside sintered silver at high temperatures. Ageing was carried out by placement on a cartridge heater or inside an oven at high temperature to monitor the changes to the microstructure. Sample set 1 was stored at high temperature after sintering without further processing steps, while sample set 2 underwent oxidizing treatment after the sintering profile by storage inside an oven at 150 °C for 24 h along with beakers containing overall 500 mL of water

in a sealed system. This process step allows steam to penetrate through the porous structure of the sintered silver, causing a reaction between the steam and sintered silver surfaces. Optical images for sample set 1 were produced before and after high temperature aging at 250 to 400 °C for up to 7 h, while the optical images for sample set 2 were produced before and after storage at 300 °C up to 603 h and aging up to 24 h at 350 to 450 °C. The optical images from these samples were then analysed using ImageJ 1.46 and the Matlab® image processing toolbox to investigate the microstructural changes of sintered silver grains. Refer to references [9, 14] for further information on the image processing techniques utilised and algorithms for extracting grain size, which references also include further information regarding the benefits and implications of observations of sintered silver microstructure through a cover-slip.

The third sample set was produced for cross-sectional analysis, and was again sintered using the recommended sintering profile. Samples 3.1 and 3.2 did not undergo oxidizing treatment, while sample 3.3 went through the same steaming process as of sample set 2. Sample 3.1 was kept as a control sample and samples 3.2 and 3.3, were then stored at 300 °C for 24 h and 124 h respectively. All samples from set 3 were mounted using a cold mounting resin and polished mechanically with silicon carbide cloths and water based diamond solutions. These samples were then observed by SEM and compared to understand whether the effects of steaming observed in sample set 2 occurred throughout the interior of the sintered silver joint. The thickness of other sample sets can be estimated from the SEM images of Sample set 3 to be around 23 µm.

While 24 h steaming has been selected as the oxidizing treatment to ensure that steam has penetrated throughout the whole sample, other oxidizing treatments may achieve the same effect. For example, Sample 4.1 was stored under water for 10 min and then was partially dried at room temperature for 24 h before being stored at 300 °C for 24 h to observe the microstructural

stabilization of this technique. Residual water would have converted to steam and contributed to oxidation via the open pore network during the storage phase. See Figure 1 for schematic representation of the processing steps for all the samples.



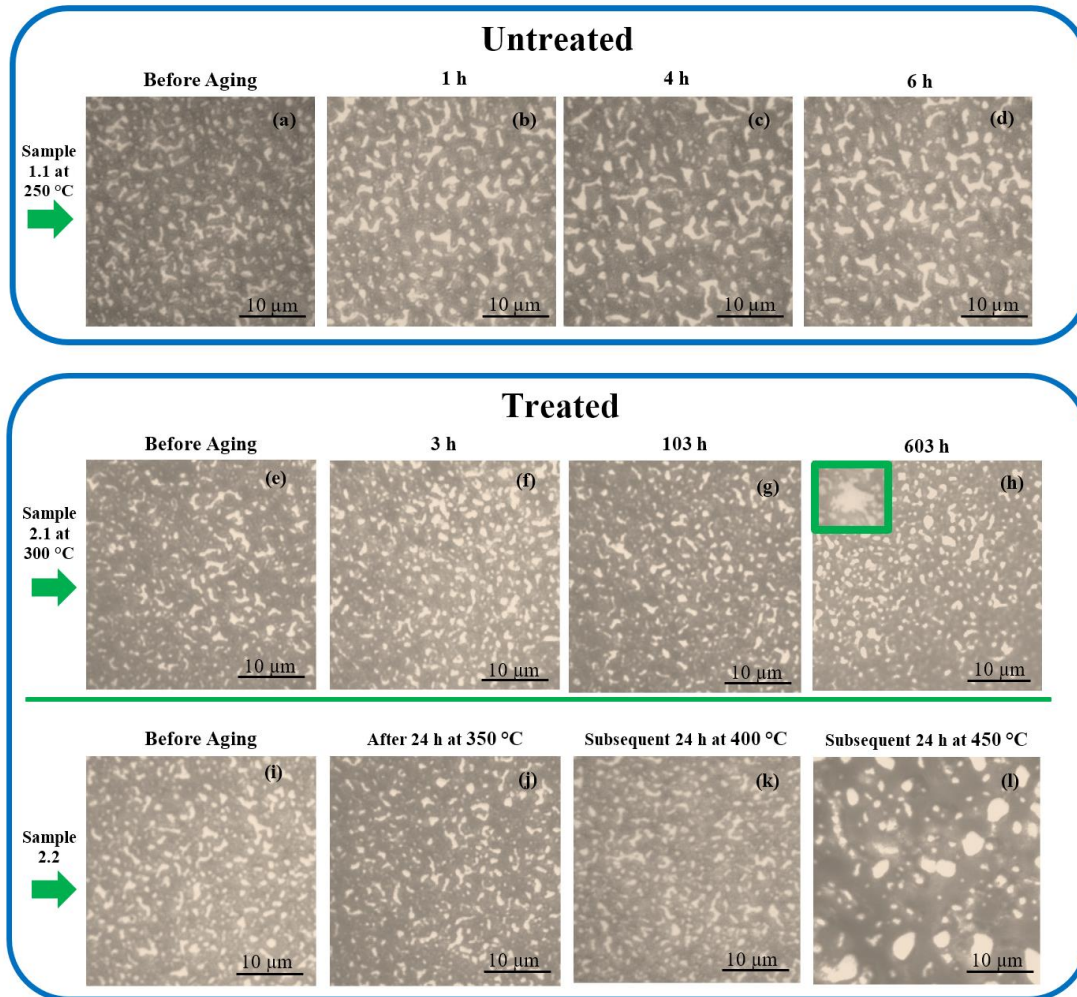
**Figure 1.** Schematic representation of sample preparation process. Steps 1 and 2 were performed for all samples and step 3 shows the additional treatment for thermal stabilization.

Table 1. Sample Sets and their Treatments			
Sample Set	Sample Number	Treatment	High Temperature Aging
1	1.1	Untreated	250 °C up to 7 h
	1.2		300 °C up to 7 h
	1.3		350 °C up to 7 h
	1.4		400 °C up to 7 h
2	2.1	Treated with Steam	300 °C up to 603 h
	2.2		350, 400, 450 °C for 24 h each
3	3.1	Untreated	No Aging (Control)
	3.2		300 °C for 24 h
	3.3	Treated with Steam	300 °C for 124 h

4	4.1	Treated with Water	300 °C for 24 h
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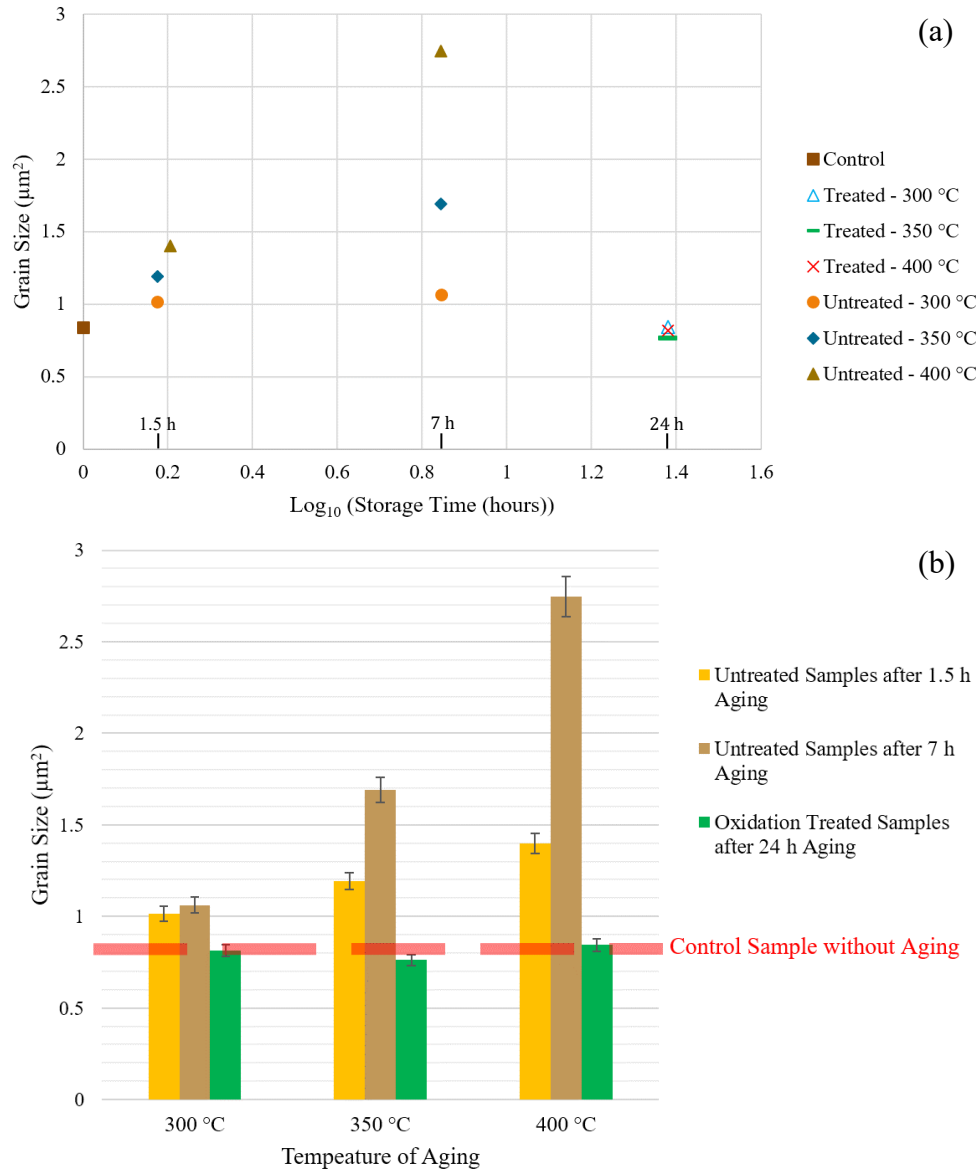
### 3. Results and Discussion

Optical images from the first and second sample sets are compared in Figure 2. Untreated samples from set 1 were only stored at their designated high temperatures for up to 7 hours since changes in microstructure were clearly visible in that timescale. Figure 2 (a-d) shows the fast microstructural evolution of sample 1.1 at 250 °C. However, the treated sample number 2.1 shown in Figure 2 (e-h) has been stored for 603 h at 300 °C and only at 603 h did a few isolated grains begin to grow. One example of such grains is inserted in top left corner of Figure 2 (h); note that this image was specifically selected to capture one of these rare grains (observed 1 in 7000 grains), while all other images in Figure 2 are from random areas. These growing grains could correspond to the small number of closed spaces expected inside sintered silver, while 96-99.9% of the pores will be part of an open network [15, 16]. Inside the closed spaces steam cannot penetrate and therefore grain growth can occur. Grain size measurements indicate that the average size of the grains at 300 °C remained constant up to 603 h; the effect of isolated grain growth being negligible. By contrast the untreated samples went through significant grain growth even at 250 °C in less than 2 h. A summary of the grain size evolution for sample set 1 and 2 are presented in Figure 3. It can be seen in this figure that 24 h storage of Sample 2.2 at 350 °C and subsequently at 400 °C results in no changes to microstructure, as seen in Figure 2 (i-k), while storage at 450 °C does result in significant grain growth, showing that the protection provided by oxidation wears off between 400 °C and 450 °C, see Figure 2 (l).



**Figure 2.** Optical images of sintered silver under cover-slip. The bright areas correspond to silver grains in contact with the cover-slip. (a-d) Untreated Sample 1.2. (e-h) Treated Sample 2.1 (image (h) contains image of a bigger grain in the top left corner from another area with the same magnification). (i-l) Treated Sample 2.2.





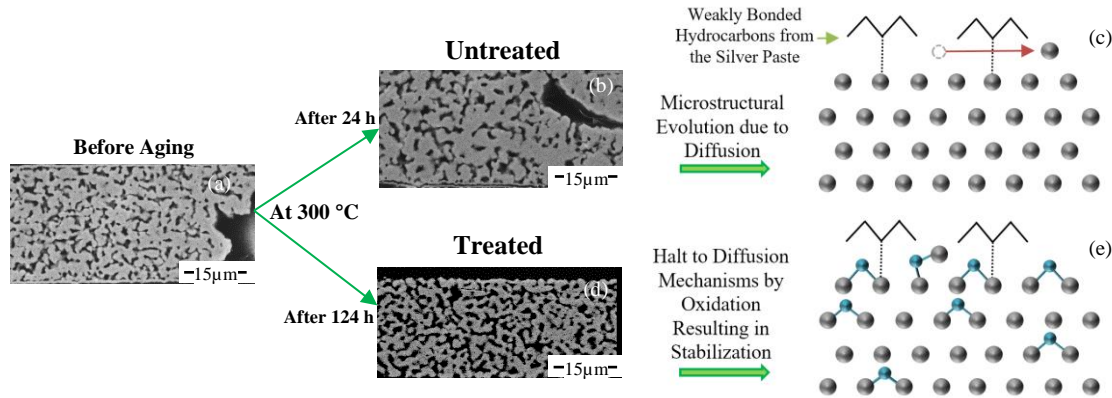
**Figure 3.** Comparison of grains sizes of treated and untreated samples. (a)

Grain size versus storage time. (b) Grain size versus temperature.

Untreated results are obtained from Sample set 1 and treated results from sample set 2.

Given that the decomposition temperature of the most stable silver oxide ( $\text{Ag}_2\text{O}$ ) is 400 °C from Differential Thermal Analysis of silver oxide ( $\text{Ag}_2\text{O}$ ) [17], and exposure of silver to air results in oxidation and halt to surface diffusion and grain growth [18], the stability after treatment can be

attributed to formation of a silver oxide passivating layer. The exterior of the air exposed sample is seen to be immediately stabilized but not the interior microstructure [9], which remains stable only after the oxidizing treatment. This is shown in Figure 4 where the microstructural stability seen in sample set 2 is seen to occur throughout the sample cross-section only in the treated case and significant grain growth can be observed for the untreated sample. As can be seen from Figure 4 (c and e) as schematic representations of the likely processes, this effect can be explained by the fact that while silver atoms inside pure silver can migrate and diffuse easily via surface diffusion, the oxidation has the effect of immobilising and pinning the silver atoms and stabilizing the structure up to the decomposition temperature of  $\text{Ag}_2\text{O}$ , which has also been observed and confirmed previously through direct exposure to atmosphere [18]. Although calculations of morphology changes driven by surface self-diffusion on pure silver are orders of magnitude faster than those observed experimentally [9], reduction of surface diffusion coefficients in the presence of organic residues from the original paste and partial oxidation can explain the discrepancy. Oxygen and humidity from air can penetrate the pore network in limited quantities without treatment, but an external oxidizing treatment with high intensity has been shown to be necessary in order to achieve thermal stability at 400 °C.



**Figure 4.** SEM images of cross-sections of sample set 3 and their microstructural evolution's underlying mechanisms. (a) Before aging, sample 3.1. (b) Untreated sample 3.1 after 24 h at 300 °C. (c) Schematic representation of easy surface diffusion mechanism of silver atoms on sintered silver. (d) Treated sample 3.3 after 124 h at 300 °C. (e) Schematic illustration of halt to diffusion as a result of oxygen atoms pinning silver atoms. The dotted lines in (c) and (d) represent weak Van der Waals type bonds and solid lines represent strong ionic bonds preventing surface diffusion.

Another simpler oxidation treatment has indicated the same stabilization effect. Sample 4.1 exhibits the same stabilization after dipping the sample in water for 10 min, in which ageing at 300 °C for 24 h results in no visible changes to microstructure.

#### 4. Conclusions

In summary, oxidizing treatment of sintered silver has resulted in increased stability and arrest of high temperature microstructural evolution up to 400 °C. While normal sintered silver undergoes significant grain growth even at 250 °C in less than 1 h, the treated samples have been stable for at least 24 h at 400 °C. At 300 °C almost the entire sample is seen to be stable up to at least 600 h, while only a few isolated grains coalesce, confirming the existence of closed pores inside sintered silver at these locations. The increased stability has been explained as a result of

oxidation of sintered silver, which enables the possibility of a broad range of possible techniques for boosting the stability temperature range of sintered silver from the existing 200 °C up to 400 °C. These patent pending techniques [19] can be applied conveniently after sintering by introducing oxidizing mechanisms such as dipping in water. The existence of simple stabilizing treatments also opens up the possibility of using higher porosity silver for large die applications where the stress exerted on the die is a limiting factor. While the stabilisation technique utilised here has been demonstrated only for the NBE Tech pastes, the mechanism should hold generally but further work is needed to establish this.

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